

FORM PTO-1390 (Modified)
(REV 10-95)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

0160-0193-0 PCT

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/463961

INTERNATIONAL APPLICATION NO.
PCT/JP98/04666INTERNATIONAL FILING DATE
15 OCTOBER 1998PRIORITY DATE CLAIMED
17 OCTOBER 1997

TITLE OF INVENTION

PROCESS AND APPARATUS FOR TREATING SEMICONDUCTOR PRODUCTION EXHAUST GASES

APPLICANT(S) FOR DO/EO/US

Hiroshi IKEDA, et al

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☐ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

Notice of Priority

PCT/IB/304

PCT/IB/308

Drawings (4 sheets)

Amended Sheets 25, 25/1, 26

Request For Consideration of Documents Cited in International Search Report

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.492(a)(1) - (5)) : <div style="font-size: 24pt; font-weight: bold; text-align: center;">09/463961</div>		INTERNATIONAL APPLICATION NO. <div style="font-weight: bold; text-align: center;">PCT/JP98/04666</div>		ATTORNEY'S DOCKET NUMBER <div style="font-weight: bold; text-align: center;">0160-0193-0 PCT</div>	
---	--	---	--	---	--

20. The following fees are submitted:.. BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : <input checked="" type="checkbox"/> Search Report has been prepared by the EPO or JPO \$840.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) \$670.00 <input type="checkbox"/> No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$760.00 <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$970.00 <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$96.00 <div style="text-align: center; margin-top: 10px;">ENTER APPROPRIATE BASIC FEE AMOUNT =</div>				CALCULATIONS PTO USE ONLY <div style="border: 1px solid black; height: 100px; width: 100%;"></div>	
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30				<div style="border: 1px solid black; padding: 5px;">\$840.00</div> <div style="border: 1px solid black; padding: 5px;">\$130.00</div>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	- 20 =	0	x \$18.00	\$0.00	
Independent claims	- 3 =	0	x \$78.00	\$0.00	
Multiple Dependent Claims (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$970.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable). <input type="checkbox"/>				\$0.00	
SUBTOTAL =				\$970.00	
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30				\$0.00	
TOTAL NATIONAL FEE =				\$970.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable). <input type="checkbox"/>				\$0.00	
TOTAL FEES ENCLOSED =				\$970.00	
				Amount to be: refunded	\$
				charged	\$

☒ A check in the amount of **\$970.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees.
 A duplicate copy of this sheet is enclosed.

☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **15-0030** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

OBLON, SPIVAK, McCLELLAND, MAIER & NEUSTADT, P.C.
 Crystal Square Five, Fourth Floor
 1755 Jefferson Davis Highway
 Arlington, Virginia 22202
 US

 Telephone Number (703) 415-3000
 Facsimile Number (703) 415-2250

WILLIAM E. BEAUMONT

REGISTRATION NUMBER 30,996

SIGNATURE

Norman F. Oblon

NAME

24,618

REGISTRATION NUMBER

DATE

February 10, 2000

09/463961
PTO/PCT Rec'd 09 MAR 2000

0160-0193-0 PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF: :
HIROSHI IKEDA ET AL : ATTN: APPLICATION DIVISION
SERIAL NO: 09/463,961 :
FILED: February 10, 2000 :
FOR: PROCESS AND APPARATUS FOR
TREATING SEMICONDUCTOR
PRODUCTION EXHAUST GASES

COPY

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as follows.

Claim 5, lines 1-2, replace "any one of Claims 1 to 4" with --Claim 1--.

Claim 6, lines 1-2, replace "any one of the Claims 1 to 5" with --Claim 1--.

Claim 7, lines 1-2, replace "any one of Claims 1 to 7" with --Claim 1--.

005250 "T95E9460

REMARKS

Claims 1-8 are active in this application.

Claims 5-7 have been amended to remove multiple dependencies. No new matter is believed to have been added to this application by these amendments.

Applicants submit that the present application is ready for examination on the merits. Early notice to this effect is earnestly solicited.

Respectfully submitted,

OBLON, SPIVAK, McCLELLAND,
MAIER & NEUSTADT, P.C.



Norman F. Oblon
Attorney of Record
Registration No. 24,618

James J. Kelly, Ph.D.
Registration No. 41,504

Crystal Square Five - Fourth Floor
1755 Jefferson Davis Highway
Arlington, VA 22202
(703) 413-3000
Fax #: (703) 413-2220
NFO.JK

I:\atty\JK\01600193.PR

SPECIFICATION

PROCESS AND APPARATUS FOR TREATING
SEMICONDUCTOR PRODUCTION EXHAUST GASES

FIELD TO WHICH THE INVENTION BELONGS

5 The present invention relates to a treatment of exhaust gases, and in particular, relates to a process and an apparatus for removing harmful components from exhaust gases discharged from a semiconductor production device.

PRIOR ARTS

10 In the present semiconductor production industry, CF_4 , CHF_3 , C_2F_6 , Cl_2 , HBr , HCl , BCl_3 , ClF_3 and the like are employed in the processes of dry etching of silicon wafers and chamber cleaning, and tetraethoxysilane (hereinafter referred to as TEOS), NH_3 , SiH_2Cl_2 and the like are employed
15 in the CVD process of a silicon wafer. Exhaust gases of these processes include the above unreacted gases, as well as decomposition products such as SiF_4 , F_2 , HF , $SiCl_4$, CH_3CHO , CH_3OH and C_2H_5OH which exhaust gases cannot be discharged as they are and hence are discharged after harmful components
20 are removed by a removing apparatus.

Removing apparatus are roughly classified into two types such as dry type apparatus employing a solid adsorbent and wet type apparatus employing a chemical liquid.

Conventional removing apparatus for semiconductor
25 production exhaust gases have the following problems.

(In the Case of Dry Type Apparatus)

Generally, they can achieve a high treatment performance and can adjust the concentration of harmful

components at the removal outlet to a low concentration acceptable for working circumstances, but have the following problems.

(1) It is necessary to replace a solid adsorbent by fresh one whenever it is exhausted, and hence, the running cost thereof is high.

(2) In the case of an exhaust gas containing a solid reaction product, blocking may occur at times.

(3) Since the used or exhausted adsorbent contains highly concentrated harmful components, the treatment of the adsorbent is time consuming and is very costly. In addition, due to a high concentration of the components, troubles such as heat generation may occur at times.

(In the Case of Wet Type Apparatus)

Generally, the running cost thereof is low, but they have the following problems.

(1) In the case of ordinary wet type apparatus, they have a low treatment performance, and it is hard to reduce the concentration of harmful components at the removal outlet to an acceptable level for working circumstances. Besides, there are a smaller number of components which can be treated.

(2) In the case of ordinary wet type apparatus, solid reaction products (e.g., NH_4Cl , SiO_2 , B_2O_3) may be produced at a posterior stage of the apparatus which products may cause blocking.

(3) In the case of ordinary bubble columns, the exhaust gas in the inlet side comes to have a positive pressure and a

high load may be exerted on a vacuum pump or the like installed at the upstream side.

(4) In the case of jet scrubber type apparatus, trouble may occur in which a gas is raised onto a solid product by a circulating pump.

Moreover, since these removing apparatus may be installed inside a clean room, restrictions such as the fact that they should not be a source of the contamination in the clean room are imposed.

10 SUMMARY OF THE INVENTION

It is the object of the present invention to solve the above problems and to provide a process and an apparatus for treating semiconductor production exhaust gases, characterized in that a high removal rate of harmful components from exhaust gases is maintained, blocking due to a solid product can be prevented, and the running cost is low.

According to one aspect of the present invention, a process for treating exhaust gases is provided, which process comprises a step of introducing exhaust gases into an aqueous alkaline liquid in an aeration stirring tank while stirring the aqueous alkaline liquid, and a step of further removing harmful gases from the gases discharged from the aeration stirring tank.

In the present invention, the above removal step preferably comprises a step of allowing the gases discharged from the aeration stirring tank to come into contact with an aqueous liquid. Or, the above removal step preferably

comprises a step of introducing the gases which have been discharged from the aeration stirring tank into a packed column filled with treating agent. Alternatively, the above removing process preferably comprises a step of allowing
5 the gases discharged from the aeration stirring tank to come into contact with an aqueous liquid, and a step of introducing the gases discharged from the aeration stirring tank into a packed column filled with a treating agent.

It is preferable that the above aqueous alkaline
10 liquid is an aqueous solution containing no alkaline metal element and that the pH of said aqueous solution is from 7.1 to 10.

In addition, it is preferable that the gases discharged from the aeration stirring tank are transferred
15 by a gas transfer device. As the gas transfer device, a gas suction device to be installed at the downstream of a gas-liquid contact device or a packed column can be exemplified. However, a fan may be installed as the gas transfer device at the upstream of the gas-liquid contact
20 device or the packed column.

The process preferably comprises further a step of discharging exhaust gases from the semiconductor production apparatus, said exhaust gases being introduced into the above aqueous alkaline liquid in the above introduction step.

25 According to another aspect of the present invention, an apparatus for treating exhaust gases is provided, which comprises

an aeration stirring tank for introducing exhaust

gases into an aqueous alkaline liquid while stirring the aqueous alkaline liquid; and

at least one of a gas-liquid contact device for allowing gases discharged from said aeration stirring device
5 to come into contact with the aqueous liquid and a packed column filled with an agent for passing gases discharged from said aeration stirring device.

In the present invention, the apparatus preferably comprises said gas-liquid contact device. Or, in the
10 present invention, the apparatus preferably has said packed column. Or the apparatus preferably comprises said gas-liquid contact device and said packed column.

In addition, the apparatus preferably comprises a gas transfer device for transferring gases which have passed
15 through the aeration stirring tank.

Moreover, the apparatus preferably comprises a passage for introducing exhaust gases discharged from the semiconductor production apparatus into said aeration stirring tank.

20 According to the present invention, acid gases such as HCl and HF, organic silicon compounds such as tetraethoxy silicon, and inorganic halogen compounds such as BCl₃ and SiCl₄ can be removed in the aeration stirring tank.

Besides, in the present invention, harmful gases which
25 have failed to be removed by the aeration stirring tank, for example, alkaline gases such as ammonia and amine, water-soluble organic compounds such as ethanol and acetoaldehyde, halogenated silicon compounds such as SiCl₄, and halogen

gases such as F_2 and Cl_2 can be removed by the gas-liquid contact device or the packed column at a posterior stage. Very small amounts of acid gases such as HCl and HF may pass through the aqueous alkaline liquid at times, and such very small amounts of acid gases can also be removed at a posterior stage.

The gas-liquid contact device is particularly suitable for removing water-soluble organic compounds, acid gases and alkaline gases. On the other hand, the packed column filled with a treating agent is particularly suitable for removing halogenated silicon compounds and halogen gases.

The present invention does not intend to remove organic fluorine compounds such as CF_4 , CHF_3 and C_2F_6 . This is because these organic fluorine compounds are chemically stable and do not significantly affect semiconductor production.

According to the present invention, in the process for treating exhaust gases by allowing semiconductor production exhaust gases to come into contact with an alkaline solution, thereby removing harmful components, it is possible to conduct the bringing into contact of said exhaust gases with the alkaline solution in the aeration stirring tank, and allow the gases after contact to come into further contact with water, as well as, bring these gases into contact with the solution by gas suction at a posterior stage.

Moreover, according to the present invention, in the apparatus for treating exhaust gases by allowing semiconductor production exhaust gases to come into contact

with an alkaline solution, thereby removing harmful components, it is possible to employ an aeration stirring tank for allowing the exhaust gases to come into contact with the alkaline solution and a gas-liquid contact device for allowing exhaust gases from the stirring tank to come into contact with water, and further install a gas suction device for sucking gases at a stage posterior to these devices.

In the present invention, exhaust gases can be contact with treating agent in a packed column filled brought into with the agent; in addition, the pH of said alkaline solution is preferably adjusted to from 7.1 to 10, in particular, from 8.0 to 9.5, employing an aqueous solution containing no alkaline metal elements such as an aqueous ammonia or amine.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a diagram showing the whole constitution of an embodiment of a treating apparatus according to the present invention.

Fig. 2 is a diagram showing the whole constitution of another embodiment of a treating apparatus according to the present invention.

Fig. 3 is a whole constitution view showing still another embodiment of a treating apparatus according to the present invention.

Fig. 4 (a) and Fig. 4 (b) are cross sections of an aeration stirring tank to be employed in the present invention.

Fig. 5 (a) and Fig. 5 (b) are cross sections of a gas-liquid contact device to be employed in the present invention.

Fig. 6 is a diagram showing the whole constitution of another embodiment of a treating device according to the present invention.

PREFERRED EMBODIMENTS OF THE INVENTION

The present invention will be described below in detail by making reference to drawings.

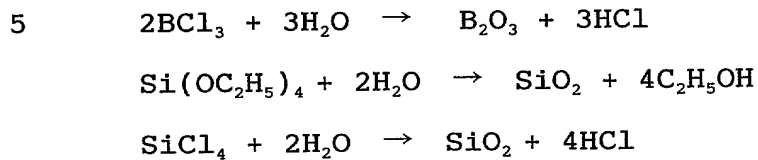
Each of Fig. 1 to Fig. 3 shows a whole constitution diagram of an apparatus for treating semiconductor production exhaust gases according to the present invention. In Fig. 1 to Fig. 3, 1 shows a semiconductor production exhaust gas, 2 an overflow pipe, 3 an alkaline liquid, 4 a washing liquid (alkaline solution), 5 an aeration stirring tank, 6 an alkali-treated exhaust gas, 7 a gas-liquid contact device, 8 water, 9 and 16 a demister, 10 a drainage pipe, 11 a packed column, 12 a suction device, 13 a treated gas, 14 a pH measuring instrument, and 15 water.

First of all, the present invention will be described by making reference to Fig. 1.

Fig. 1 shows an example with no packed column provided therein; the semiconductor production exhaust gas 1 is, first of all, allowed to come into contact with the alkaline washing liquid 4 with a pH adjusted to from 7.1 to 10, preferably from 8.0 to 9.5, with the water 15 or the alkaline solution 3 in the aeration stirring tank 5. Here, the majority of components to be removed are absorbed in the

washing liquid and removed.

The compounds are hydrolyzed in the aqueous alkaline liquid, for example, according to the following reaction:



10 In addition, acid gases such as HF, HCl and HBr are absorbed in the aqueous alkaline liquid.

As the alkaline solution, aqueous solutions of ordinary alkaline materials can be employed; however, since alkaline metal elements such as Na and K contained in sodium hydroxide and potassium hydroxide act as harmful components
15 in semiconductor production even in extremely small amounts thereof, it is preferable, if possible, to employ an alkaline liquid containing no alkaline metal elements such as ammonia, carbonates of ammonia, phosphates of ammonia and amine.

20 As the aeration stirring tank 5, tanks as illustrated in Fig. 4 (a) and Fig. 4 (b) can be employed. They disperse a gas by rotating a stirring blade at a high speed in a liquid. The aeration stirring tank preferably comprises a tank for retaining the alkaline liquid, a stirring means
25 for stirring the alkaline liquid, and an exhaust gas introduction part for introducing the exhaust gas into the alkaline liquid. The stirring means comprises, for example, a motor, a shaft to be connected to the motor rotatably, and

005550" 1963460
a blade attached to the shaft. The exhaust gas is introduced into the alkaline liquid from the outlet of the exhaust gas introduction part. The outlet of the exhaust gas introduction part is preferably near the blade of the stirring means.

In Fig. 4 (a), Fig. 4 (b), Fig. 5 (a) and Fig. 5 (b), 17 shows a motor, 18 a stirring blade, 19 a gas introduction direct pipe, 20 a baffle, 21 a porous pipe, 22 a filling, 22 a spray nozzle, 24 an exhaust gas washed with water, and 25 air.

Fig. 4 (a) shows a device wherein the stirring blade 18 (disc turbine blade) with two or more right-angled turbine blades attached to the disc-like circumference, which is directly connected to the motor 17, is rotated in a liquid at a high speed, a gas is introduced by the direct pipe 19 from immediately below the stirring blade, and the gas is turned into fine foam by the shear force of the stirring blade to disperse the liquid; moreover, the stirring blade is preferably provided in two steps upward and downward and rotated at a high speed with a view to increasing the retention time of the foam in the liquid and the shear force of the stirring blade.

Fig. 4 (b) shows a device wherein the stirring blade 18 (disc turbine blade), which is directly connected to the motor 17, and has several right-angled turbine blades attached to the disc-like circumference, is rotated in a liquid at a high speed, a gas in the form of fine bubbles is introduced by the porous pipe 21 from right below the

00550" 1355460

stirring blade, and the gas is divided into finer foam by the shear force of the stirring blade provided right overhead to disperse the liquid. 20 shows a baffle.

The reason why the aeration stirring tank is employed in this way in the present invention will be described hereunder.

In the case of treating a high-concentration acid gas with an alkaline liquid in a liquid dispersion type wet absorption device such as a packed column generally and widely employed, a mist containing a salt produced by a neutralization reaction is formed. For example, when a HCl-containing gas is treated with ammonia water as a neutralization liquid, a mist containing NH_4Cl is formed. Besides, when sodium hydroxide is employed as a neutralization liquid, a mist containing NaCl is formed. When BCl_3 and SiF_4 are wet-treated, a mist containing B_2O_3 or SiO_2 which is a hydrolyzed product thereof is formed. Since these products may be deposited at a stage posterior to the treatment device and cause trouble such as blocking, it is necessary to prevent their formation.

It is guessed that these mists are produced by a reaction of treatment object components with fine particles of a washing liquid present in the absorption device and components volatilizing from the washing liquid (for example, a water molecule and an ammonia molecule). In general, while the diffusion coefficient of a gaseous molecule is of the order of $10^{-5} \text{ m}^2/\text{sec}$, the diffusion coefficient of these mists is said to be of the order of 10^{-3} to $10^{-11} \text{ m}^2/\text{sec}$, and

thus, the diffusion rate is extremely slow.

00550" 1955460

In general, in a wet absorption device, as a result of treating object components dissolved in a liquid, the concentration of the gas phase at the gas-liquid interface decreases, and a concentration gradient occurs in the gas phase nearby. The treatment object components are dispersed and transported by this concentration gradient, and the dissolution of the treatment object components into the liquid is accelerated. The transport amount by diffusion is in proportion to the diffusion coefficient of the treatment object components. However, since the diffusion coefficient of the mists are extraordinarily small in comparison with that of a gaseous molecule as described above, the transport amount by diffusion becomes extraordinarily small.

Therefore, the dissolution rate of mist components into a liquid film is slow and sufficient removal performance cannot be obtained.

Hence, in order to sufficiently remove the resultant mists by the dissolution thereof into the liquid, it is necessary to accelerate the dissolution of the mists through a mechanism other than diffusion transport.

In the present invention, a device capable of obtaining a high removal performance is obtained by accelerating the renewal of a gas-liquid interface by finely dividing foam in a liquid by a stirring blade and accelerating dissolution by maintaining the mist concentration high in the gas phase at the gas-liquid interface.

Subsequently, since the gas 6 coming out of the

004494 05500
aeration stirring tank 5 contains mainly treatment object components which have been failed to be removed, or ammonia and amine in the case of employing a volatile alkaline liquid, it is allowed to come into contact with water 8 in a
5 suitable gas-liquid contact device 7, and then droplets are removed by the demister 9.

As the gas-liquid contact device to be employed here, any appropriate known device can be employed, and for example, those described in Fig. 5 (a) and Fig. 5 (b) may be
10 employed.

Fig. 5 (a) shows a packed column filled with a Raschig ring 22 in the inside thereof. Water 8 is sprayed from the upper part of the Raschig ring 22 onto the top of the filling, and the gas 6 is subjected to gas-liquid contact
15 when it passes the filling zone.

Fig. 5 (b) shows a shower column equipped inside thereof with a spray nozzle 23. Water 8 is sprayed in the form of a water film from the tip of the spray nozzle 23, and the gas is subjected to gas-liquid contact when it
20 passes through the water film.

Water after subjected to the gas-liquid contact is discharged from the drainage pipe 10. Here, most of ammonia and amine are absorbed, and their concentration is reduced to an amount which is lower than the acceptable
25 concentration for working circumstances.

The treated gas passes the suction device 12 and is discharged from the device as shown line 13. As an example of the suction device 12 an ejector type suction device can

be employed, wherein high-pressure air or water is jetted from a nozzle and by suction force generated there, the pressure of the secondary side becomes negative; a fan and a water seal pump can also be employed.

5 The suction device is not an indispensable device, and the pressure of the primary side may be made positive instead of the pressure of the secondary side being made negative. For example, it is possible to provide a fan on the primary side and introduce a gas.

10 The washing liquid 4 is consumed by carrying out the treatment, and the removal efficiency thereof is decreasing. Hence, it is preferred that the pH is monitored by using a pH electrode 14, if necessary, and that the alkaline liquid 3 is injected into the washing liquid by an agent-injecting
15 pump when the pH is lowered than the predetermined level.

 In addition, reaction products of components in an exhaust gas with components in water or an alkaline liquid may be accumulated in a washing liquid to cause a decrease in a removal efficiency and the deposition of the products.
20 Hence, it is preferable that the washing liquid is discharged from the overflow pipe 2 while adding a certain amount of water 15 to prevent the accumulation of the reaction products.

 The aeration stirring tank 5 has been described above
25 wherein a disc turbine type blade is rotated, a gas is dispersed by the shear force generated therefrom, the shear force is increased by providing blades on two upward and downward layers and the retention time of the gas in the

washing liquid is extended. However, any stirring blade other than the above may be employed so far as it can provide a sufficient gas-liquid contact efficiency.

As the gas-liquid contact device 7, any types of the device may be employed provided that they can perform a sufficient gas-liquid contact efficiency, and the suction device 12 may be of any type other than the above so far as the pressure of the inlet exhaust gas 1 is constantly maintained negative.

In Fig. 2 and Fig. 3, the packed column 11 filled with an agent is added to the apparatus of Fig. 1; in Fig. 2, the packed column 11 is provided at a stage subsequent to the gas-liquid contact device 7, and in Fig. 3, the packed column 11 is provided at a stage prior to the gas-liquid contact device 7.

In Fig. 2, when treatment object components which have failed to be removed by the treatment of Fig. 1 remain, they are adsorbed to remove by the packed column 11 filled with an appropriate agent at a level below the acceptable concentration for working circumstances.

In Fig. 3, the gas 6 which has been subjected to droplet removal by the demister 16 after coming out of the aeration stirring tank 5 contains mainly treatment object components which remain unremoved, or contains ammonia, amine and the like when a volatile alkaline liquid is employed. Then, gas 6 is, first of all, allowed to pass the packed column 11 filled with an appropriate agent, and the treatment object components are adsorbed on the agent to be

removed at a level below the acceptable concentration for working circumstances. Here, most of the treatment object components which have failed to be removed by the aeration stirring tank 5 are removed, but ammonia and amine may remain at times. Hence, the gas is then allowed to come into contact with water 8 in a suitable gas-liquid contact device 7, thereby ammonia and amine are almost absorbed in the water, and the treated gas passes the suction device 12 and is discharged from the device as shown by line 13.

10 Examples of the agent to be fed into the packed column include (A) activated carbons such as alkali-added activated carbons, (B) one or more metal oxides selected from oxides of metals such as Cu, Mn, Fe and Zn, (C) anion exchange resins, and (D) soda lime. (A) Alkali-added activated
15 carbons are effective for removing SiF_4 , NO_2 , Cl_2 and NH_4Cl , and (B) metal oxides are effective for removing SiF_4 , NO_2 and NH_4Cl . As the metal oxides, for example, Cu-Mn composite oxides and oxides of transition metals such as Fe_2O_3 can preferably be employed. (C) Anion exchange resins
20 are effective for removing SiF_4 , Cl_2 and NH_4Cl . Anion exchange resins may preferably have a quaternary ammonium group. In addition to anion exchange resins, cation exchange resins alone, or both cation exchange resins and anion exchange resins may be employed, if desired. As the
25 soda lime, for example, powder of Na_2CO_3 covered with a NaOH coat can be employed.

Fig. 6 shows an apparatus comprising an aeration stirring tank 5 and a packed column 11 filled with an agent

installed downstream in the tank. The apparatus of Fig. 6 has no gas-liquid contact device 7. In the apparatus of Fig. 6, the aeration stirring tank 5 may preferably employ an alkaline solution other than ammonia. This is because when employing the agent, the removal of ammonia may be limited. In the case of employing a suitable cation exchange resin in the packed column, however, ammonia can also be removed.

Halogenated silicon compounds such as SiF_4 , and halogen gases such as F_2 and Cl_2 can be removed by the packed column filled with one of the agent.

As the packed column filled with the agent, a conventional packed column can be employed. For example, the packed column described in "Process for Removing Nitrogen Oxides in Exhaust Gases" of International Application PCT/JP98/01654, which was filed on April 10, 1998, can be employed. In addition, the packed column described in "Process for Treating Exhaust Gases Containing Inorganic Halogenated Gases" of Japanese Patent Application No 10-168572, which was filed with the Japanese Patent Office on June 16, 1998, can also be employed. The disclosure of International Application PCT/JP98/01653 and Japanese Patent Application No 10-168572 is incorporated in the present application by reference.

Examples

Hereunder, the present invention will be illustrated specifically by to examples.

Example 1

Employing a treating apparatus shown in Fig. 2, an

exhaust gas discharged from an Al etching device for semiconductor production was treated. The flow rate of the semiconductor exhaust gas was 40 l/min.

00550 "T6E9460
09463961 052300

The semiconductor exhaust gas 1 was, first of all, introduced into an aeration stirring tank 5 filled with water 4, the pH of which was adjusted to from 8.5 to 9.5 with the addition use of ammonia water 3. The introduced gas was then finely divided by a stirring blade 18 rotated with a motor 17 and came into contact with water 4. The rotation speed of the stirring blade 18 was set at 600 rpm. In order to prevent products from accumulating in the water 4, water 15 was introduced at a rate of 3 l/min into the aeration stirring tank, and the same amount of a blow-down drain 2 was drained. The pH of the blow-down drain was constantly monitored by a pH electrode 14, and the ammonia water 3 was injected when the pH was below 9.

The aeration stirring tank outlet gas 6 coming out of the aeration stirring tank was passed through water shower 7 sprayed from a spray nozzle 23 at a flow rate of 5 l/min, and allowed to come into contact with water 8. Water after contact was discharged as a water shower drain 10. A demister 9 was provided at the outlet of the water shower in order to prevent the sprayed water from the spray nozzle 23 from flying into subsequent stages. The water shower outlet gas 24 coming out of the water shower was introduced into the packed column 11 which had been filled with 10 l of an anion exchange resin. The packed column outlet gas coming out of the packed column was introduced into an air ejector

12 to be driven by air 25 and discharged as a treated gas 13.
The amount of air 25 introduced was determined to 40 l/min.

The gas treatment was performed in an apparatus having
the above constitution, and the semiconductor exhaust gas 1,
5 the aeration stirring tank outlet gas 6, the water shower
outlet gas 24 and the treated gas 13 were analyzed. The
results are shown in Table 1.

For comparison, the same exhaust gas was treated by
employing ammonia water for adjusting a pH, and a packed
10 column type scrubber a Raschig ring as a filler. Other
conditions were the same as those in Example. The results
of the treatment are shown in Table.

Table 1

	1)	2)	3)	4)	5)
BCl_3 (unit: ppm)	5000	< 1	< 1	< 1	< 1
Cl_2 (unit: ppm)	3000	2	2	< 0.5	3
AlCl_3 (unit: ppm)	10	< 1	< 1	< 1	< 1
NH_3 (unit: ppm)	< 1	50	< 1	< 1	
B_2O_3 (mg/m ³)	< 1	15	10	< 1	300
NH_4Cl (mg/m ³)	< 1	20	15	< 1	400

- 00463964 032300
- 1) Semiconductor exhaust gas 1
 - 2) Aeration stirring tank outlet gas 6
 - 3) Water shower outlet gas 24
 - 4) Treated gas 13
 - 5) Packed column type scrubber

BCl₃, Cl₂ and AlCl₃ contained in the exhaust gas were treated at each stage, and thereby the concentration of each of these components in the treated gas was below a detection limit. Besides, components such as NH₃, B₂O₃ and NH₄Cl generated during the process of the treatment were treated by the water shower and the adsorption column to lower the concentration below their detection limits.

In the case where the treatment was performed by the packed column scrubber, B₂O₃ and NH₄Cl leaked by 300 mg/m³ and 400 mg/m³, respectively. In contrast, in the case of treatment by the aeration stirring tank, the leak concentrations of B₂O₃ and NH₄Cl were 15 mg/m³ and 20 mg/m³, respectively, which are lower by one or more orders as compared with the case of the packed column scrubber.

Example 2

The treatment was conducted continuously for one month, and no trouble such as blocking in the apparatus due to solids contained in the semiconductor exhaust gas and heat release occurred. Moreover, the inside of the duct of the device outlet was checked after completion of the treatment, no adhesion of powders such as B₂O₃ and NH₄Cl was observed.

Example 3

Changes in the inlet pressure of the apparatus when changing the flow rate of air 25 to be introduced into the air ejector 12 in the constitution as shown in Example 1 are shown in Table 2. As the amount of air introduced increases, the inlet pressure decreases; An introduction of 40 l/min achieved, an inlet pressure of -150 mmAq.

Table 2

Flow rate of air introduced into air ejector (l/min)	Apparatus inlet pressure (mmAq)
0	+600
10	+300
20	+100
30	-50
40	-150

Example 4

By employing a treating apparatus shown in Fig. 3, a semiconductor exhaust gas discharged from an Al etching device for semiconductor production was treated. The flow rate of the exhaust gas was 120 l/min.

The semiconductor exhaust gas 1 was, first of all, introduced into an aeration stirring tank 5 filled with water 4, the pH of which was adjusted to from 8.5 to 9.5 with use of ammonia water 3. The introduced gas was then finely divided by a stirring blade 18 rotated with by a motor 17 and came into contact with water 4. The rotation speed of the stirring blade 18 was set at 600 rpm. In order

to prevent the accumulation of the products in water 4, water 15 was introduced at a rate of 3 l/min into the aeration stirring tank, and the same amount of a blow-down drain 2 was drained. The pH of the blow-down drain was constantly monitored by a pH electrode 14, and the ammonia water 3 was injected when the pH became below 9.

The aeration stirring tank outlet gas 6 coming out of the aeration stirring tank was introduced into a packed column 11 which had been filled with 10 l of an anion exchange resin. The packed column outlet gas coming out of the packed column was pass through water shower 7 sprayed from a spray nozzle 23 at a flow rate of 5 l/min and allowed to come into contact with water 8. Water after the contact was discharged as a water shower drain 10. A demister 9 was equipped at the outlet of the water shower in order to prevent from flying sprayed water from the spray nozzle 23 into subsequent stages. The water shower outlet gas 24 coming out of the water shower was introduced into an air ejector 12 to be driven by air 25 and discharged as a treated gas 13. The amount of the air 25 introduced was determined to 90 l/min.

The gas treatment was performed in an apparatus having the above constitution, and the semiconductor exhaust gas 1, the aeration stirring tank outlet gas 6, the packed column outlet gas and the treated gas 13 were analyzed. The results are shown in Table 3.

Table 3

	1)	2)	3)	4)
BCl_3 (unit: ppm)	5000	< 1	< 1	< 1
Cl_2 (unit: ppm)	3000	2	< 0.5	< 0.5
AlCl_3 (unit: ppm)	10	< 1	< 1	< 1
NH_3 (unit: ppm)	< 1	80	100	< 1
B_2O_3 (unit: ppm)	< 1	40	10	< 1
NH_4Cl (mg/m ³)	< 1	80	15	< 1

1) Semiconductor exhaust gas 1

2) Aeration stirring tank outlet gas 6

5 3) Packed column outlet gas

4) Treated gas 13

10 BCl_3 , Cl_2 and AlCl_3 contained in the exhaust gas were treated at each stage, and thereby the concentration of each of these components in the treated gas was reduced to a level lower than their detectable limits. Besides, components such as NH_3 , B_2O_3 and NH_4Cl generated during the process of the treatment were treated by the water shower and the packed column to lower the concentration below their

15 detection limits.

According to the present invention, the following effects can be achieved.

(1) In the above treatment process, a reaction product of treatment object components with water or an alkaline liquid is prevented from leaking at subsequent stages by employing an aeration stirring tank at an initial stage, thereby
5 troubles caused by the product can be reduced.

(2) The treating performance can be compared to that of a dry type treatment if a packed column is fitted at a subsequent stage.

(3) Since the majority of treatment object components are
10 removed at a wet treatment stage even if a packed column is fitted, the packed column has a long-life and may be of a very small size. Therefore, time required for the replacement and running cost can remarkably be reduced.

(4) Since the amount of harmful materials to be condensed in
15 the packed column is small, troubles such as heat generation do not occur easily, and the stabilization of the used agent presents no difficulties.

(5) Although the gas inlet pressure of the aeration stirring tank becomes positive, the load of a vacuum pump equipped at
20 its upstream can be reduced if a suction device is placed at a subsequent stage.

CLAIMS

1. (After the amendment) A process for treating exhaust gases, comprising

a step of equipped an aeration stirring tank having a stirring device comprising a motor, a shaft rotatably connected to the motor, and a blade attached to the shaft,

a step of introducing exhaust gases into an aqueous alkaline liquid in an aeration stirring tank while stirring the aqueous alkaline liquid, and

a step of further removing harmful gases from the gases discharged from the aeration stirring tank.

2. A process for treating exhaust gases according to Claim 1, wherein said removal step comprises a process of allowing the gases discharged from the aeration stirring tank to come into contact with an aqueous liquid.

3. A process for treating exhaust gases according to Claim 1, wherein said removing step comprises a step of introducing the gases discharged from the aeration stirring tank into a packed column filled with an agent.

4. A process for treating exhaust gases according to Claim 1, wherein said removing step comprises a step of allowing the gases discharged from the aeration stirring tank to come into contact with an aqueous liquid, and a step of introducing the gases discharged from the aeration stirring tank into a packed column filled with an agent.

5. A process for treating exhaust gases according to any one of Claims 1 to 4, wherein said aqueous alkaline liquid is an aqueous solution containing no alkaline metal element

7. A process for treating exhaust gases according to any one of Claims 1 to 7, further comprising a step of discharging exhaust gases from a semiconductor production device, said exhaust gases being introduced by the introduction step into the aqueous alkaline liquid.

8. (After the amendment) An apparatus for treating exhaust gases, comprising

an aeration stirring tank for introducing exhaust gases into an aqueous alkaline liquid while stirring the aqueous alkaline liquid; and

at least one device selected from a gas-liquid contact device for allowing gases discharged from said aeration stirring device to come into contact with the aqueous liquid, and a packed column filled with an agent for passing gases discharged from said aeration stirring device;

characterized in that said aeration stirring tank has a stirring device comprising a motor, a shaft rotatably connected to the motor, and a blade attached to the shaft.

ABSTRACT

A process and an apparatus for treating exhaust gases, comprising an aeration stirring tank (5) employing an aqueous alkaline liquid, and a gas-liquid contact device (7) and/or a packed column (11). The apparatus can remove at a posterior stage harmful gases failed to be removed by the aeration stirring tank, for example, water-soluble organic compounds such as ethanol, halogenated silicon compounds such as SiCl_4 , and halogen gases such as F_2 and Cl_2 . It is particularly suitable for purifying exhaust gases discharged from a semiconductor production device.

Fig. 1

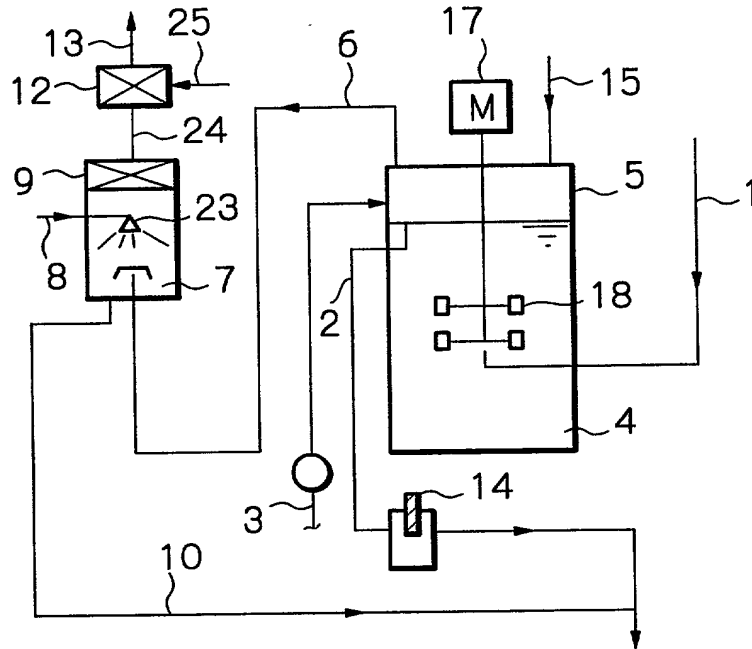


Fig. 2

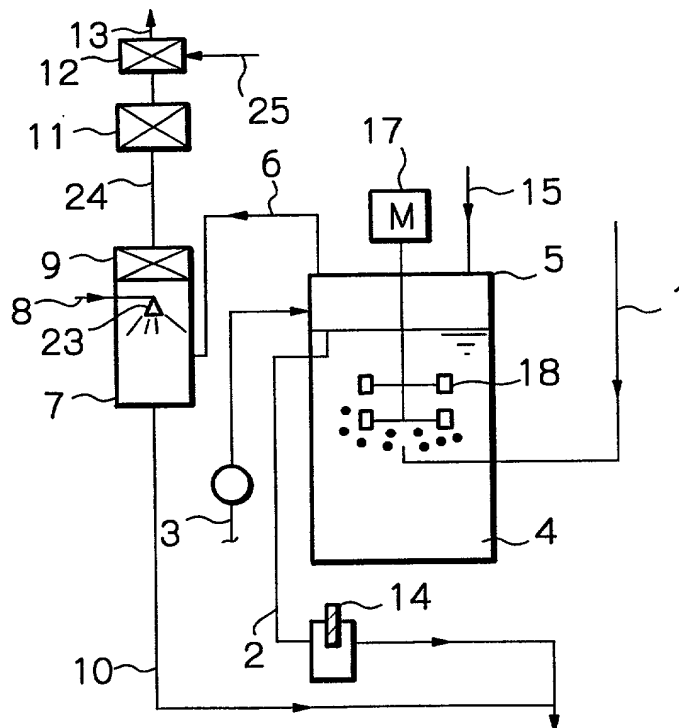


Fig. 3

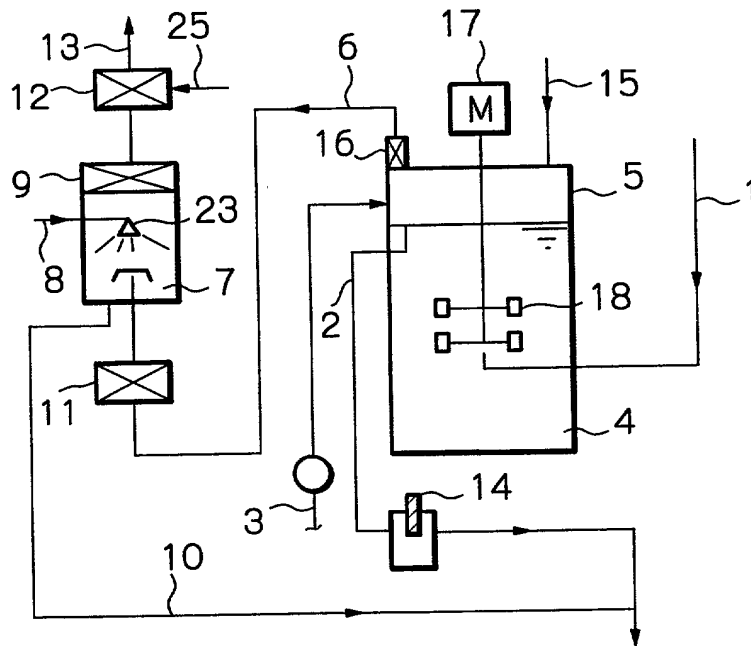


Fig. 4 (a)

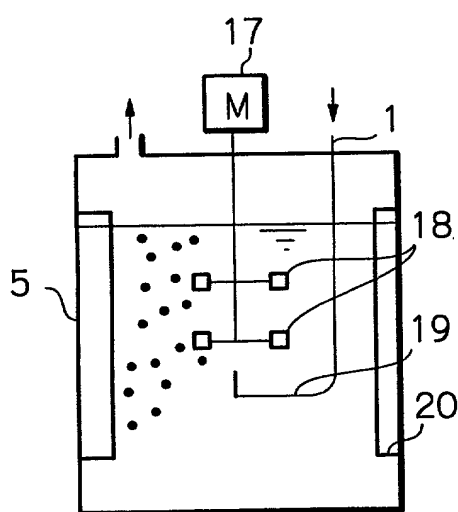


Fig. 4 (b)

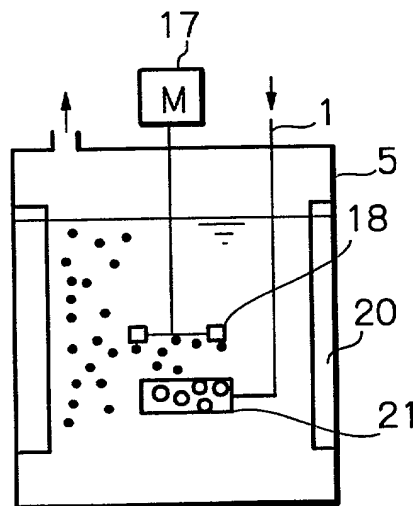


Fig. 5 (a)

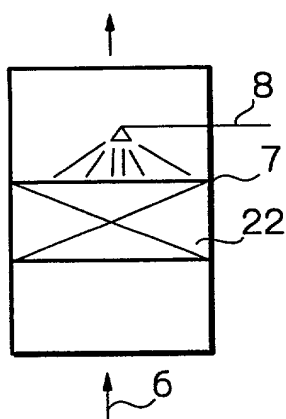
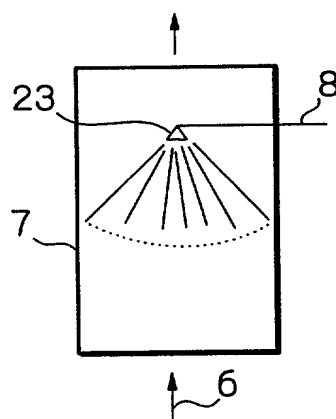
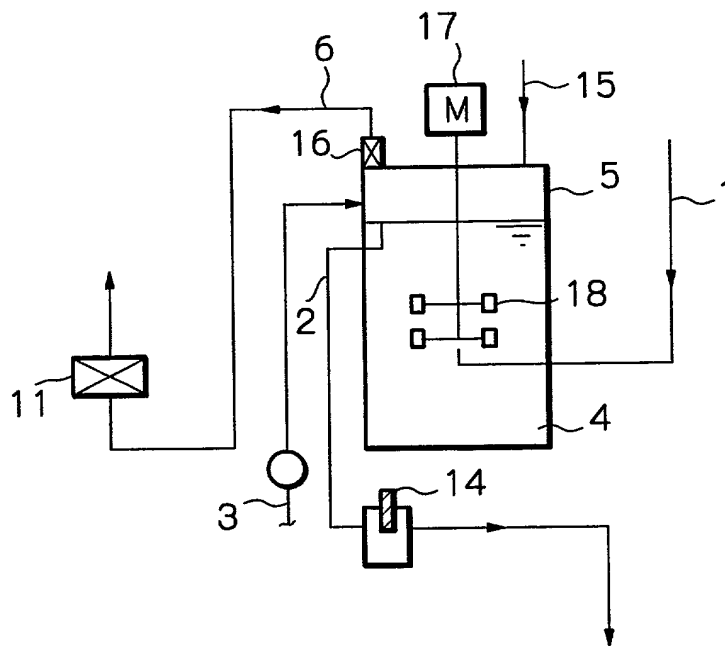


Fig. 5 (b)



09/463961

Fig. 6



Declaration, Power Of Attorney and Petition

COPY Page 1 of 3

WE (I) the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

PROCESS AND APPARATUS FOR TREATING SEMICONDUCTOR PRODUCTION EXHAUST
GASES

the specification of which

☐ is attached hereto.

☐ was filed on _____ as

Application Serial No. _____

and amended on _____.

☒ was filed as PCT international application

Number PCT/JP98/04666

on October 15, 1998,

and was amended under PCT Article ~~19~~ 34 (2)

on June 23, 1999 (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
<u>299671/1997</u>	<u>Japan</u>	<u>17/10/1997</u>	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No
_____	_____	_____	<input type="checkbox"/> Yes <input type="checkbox"/> No

We (I) hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

_____ (Application Number)	_____ (Filing Date)
_____ (Application Number)	_____ (Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.	Filing Date	Status (pending, patented, abandoned)
_____	_____	_____
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint: Norman F. Oblon, Reg. No. 24,618; Marvin J. Spivak, Reg. No. 24,913; C. Irvin McClelland, Reg. No. 21,124; Gregory J. Maier, Reg. No. 25,599; Arthur I. Neustadt, Reg. No. 24,854; Richard D. Kelly, Reg. No. 27,757; James D. Hamilton, Reg. No. 28,421; Eckhard H. Kuesters, Reg. No. 28,870; Robert T. Pous, Reg. No. 29,099; Charles L. Gholz, Reg. No. 26,395; Vincent J. Sunderdick, Reg. No. 29,004; William E. Beaumont, Reg. No. 30,996; Steven B. Kelber, Reg. No. 30,073; Robert F. Gnuse, Reg. No. 27,295; Jean-Paul Lavalleye, Reg. No. 31,451; Stephen G. Baxter, Reg. No. 32,884; Martin M. Zoltick, Reg. No. 35,745; Robert W. Hahl, Reg. No. 33,893; Richard L. Treanor, Reg. No. 36,379; Steven P. Weihrouch, Reg. No. 32,829; John T. Goolkasian, Reg. No. 26,142; Marc R. Labgold, Reg. No. 34,651; Richard L. Chinn, Reg. No. 34,305; Steven E. Lipman, Reg. No. 30,011; Carl E. Schlier, Reg. No. 34,426; James J. Kulbaski, Reg. No. 34,648; Catherine B. Richardson, Reg. No. 39,007; Richard A. Neifeld, Reg. No. 35,299; J. Derek Mason, Reg. No. 35,270; Surinder Sachar, Reg. No. 34,423; Sharon E. Crane, Reg. No. 36,113; Christina M. Gadiano, Reg. No. 37,628; Jeffrey B. McIntyre, Reg. No. 36,867; and Paul E. Rauch, Reg. No. 38,591; our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of OBLON, SPIVAK, MCCLELLAND, MAIER & NEUSTADT, P.C., whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Hiroshi IKEDA
NAME OF FIRST SOLE INVENTOR

Residence: Kanagawa, Japan

Hiroshi Ikeda
Signature of Inventor

Citizen of: Japan

Post Office Address: 1-13-17-616,
Nakamachidai, Tsuzuki-ku,

February 14, 2000
Date

Yokohama-shi, Kanagawa 224-0041 Japar

200
Yasuhiro KUBOTA

NAME OF SECOND JOINT INVENTOR

Yasuhiro Kubota

Signature of Inventor

February 14, 2000

Date

300
Takashi KYOTANI

NAME OF THIRD JOINT INVENTOR

Takashi Kyotani

Signature of Inventor

February 14, 2000

Date

NAME OF FOURTH JOINT INVENTOR

Signature of Inventor

Date

NAME OF FIFTH JOINT INVENTOR

Signature of Inventor

Date

Residence: Kanagawa, Japan

Citizen of: Japan

Post Office Address: 1-13-17-523,
Nakamachidai, Tsuzuki-ku,
Yokohama-shi, Kanagawa 224-0041 Japan

Residence: Kanagawa, Japan

Citizen of: Japan

Post Office Address: 85-1-101, Sachigaoka,
Asahi-ku, Yokohama-shi, Kanagawa,
241-0822 Japan

Residence: _____

Citizen of: _____

Post Office Address: _____

Residence: _____

Citizen of: _____

Post Office Address: _____